

**PCT**WORLD INTELLECTUAL PROPERTY ORGANIZATION  
International Bureau

## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification<sup>5</sup> :</b> <b>G03C 1/34, 7/392</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 91/11749</b> <b>(43) International Publication Date:</b> 8 August 1991 (08.08.91)
<b>(21) International Application Number:</b> PCT/EP91/00068 <b>(22) International Filing Date:</b> 12 January 1991 (12.01.91)  <b>(30) Priority data:</b> 9001487.9                      23 January 1990 (23.01.90)      GB  <b>(71) Applicant (for GB only):</b> KODAK LIMITED [GB/GB]; Patent Department, Headstone Drive, Harrow, Middlesex HA1 4TY (GB).  <b>(71) Applicant (for all designated States except GB US):</b> EASTMAN KODAK COMPANY [US/US]; Patent Department, 343 State Street, Rochester, NY 14650-2201 (US).  <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only) :</b> LEYSHON, Llewellyn, James [GB/GB]; 30 Stanbury Avenue, Watford, Herts. WD1 3HW (GB). SIDHU, Jasbir [GB/GB]; 107 Woodcock Hill, Kenton, Harrow, Middx HA3 0JJ (GB).		<b>(74) Agent:</b> BARON, Paul, Alexander, Clifford; Kodak Limited, Patent Department, Headstone Drive, Harrow, Middlesex HA1 4TY (GB).  <b>(81) Designated States:</b> AT (European patent), BE (European patent), CH (European patent), DE (European patent), DK (European patent), ES (European patent), FR (European patent), GB (European patent), GR (European patent), IT (European patent), JP, LU (European patent), NL (European patent), SE (European patent), US.  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> PHOTOGRAPHIC SILVER HALIDE MATERIALS CONTAINING A STABILISER COMPOUND  <b>(57) Abstract</b>  A colour photographic material comprising a support carrying at least one photographic silver halide emulsion layer having associated therewith a 5-, 7- or 8-chromanol image dye stabiliser.		

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	ES	Spain	MG	Madagascar
AU	Australia	FI	Finland	ML	Mali
BB	Barbados	FR	France	MN	Mongolia
BE	Belgium	GA	Gabon	MR	Mauritania
BF	Burkina Faso	GB	United Kingdom	MW	Malawi
BG	Bulgaria	GN	Guinea	NL	Netherlands
BJ	Benin	GR	Greece	NO	Norway
BR	Brazil	HU	Hungary	PL	Poland
CA	Canada	IT	Italy	RO	Romania
CF	Central African Republic	JP	Japan	SD	Sudan
CG	Congo	KP	Democratic People's Republic of Korea	SE	Sweden
CH	Switzerland	KR	Republic of Korea	SN	Senegal
CI	Côte d'Ivoire	LI	Liechtenstein	SU	Soviet Union
CM	Cameroon	LK	Sri Lanka	TD	Chad
CS	Czechoslovakia	LU	Luxembourg	TG	Togo
DE	Germany	MC	Monaco	US	United States of America
DK	Denmark				

-1-

PHOTOGRAPHIC SILVER HALIDE MATERIALS  
CONTAINING A STABILISER COMPOUND

This invention relates to photographic silver  
5 halide materials containing a stabiliser compound and  
particularly to colour photographic materials.

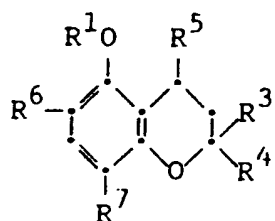
US Patent 3 591 381 describes the use of  
6-chromanols as stabilisers for azo dyes, reducing  
fade caused by light, moisture and heat. US patent  
10 4 155 765 describes O-substituted 6-chromanols used as  
photographic dye image stabilisers. US patent  
3 574 627 describes photographic dye image stabilisers  
which are 4-chromanols having 2,2-pentamethylene and  
2,2-tetramethylene rings.

15 The present invention employs related  
compounds, the 5-, 7- and 8-chromanols as stabilisers  
in photographic materials in which the image dyes, as  
is well known, are azomethine dyes. It has been found  
that not all chromanol-coupler combinations have the  
20 same properties, for example 6-chromanols have a  
deleterious effect on image dye stability when used in  
combination with yellow couplers.

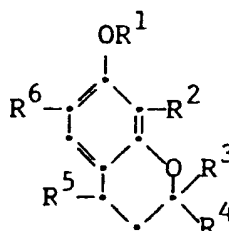
According to the present invention there is  
provided a colour photographic material comprising a  
25 support carrying at least one photographic silver  
halide emulsion layer having associated therewith a  
5-, 7- or 8-chromanol image dye stabiliser.

The preferred chromanols have one of the  
general formulae:

30

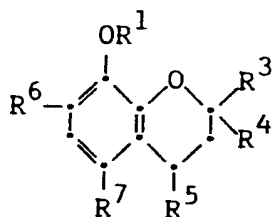


(1) 5-chromanol



(2) 7-chromanol

-2-



5

(3) 8-chromanol

wherein  $R^1$  is H, alkyl, substituted alkyl  
 (including arylalkyl, eg benzyl), preferably  
 wherein the alkyl groups have 1-4 carbon  
 atoms, or  $-R^8-COOR$ ,

10

$R$  is an alkyl, preferably having 1-4 carbon  
 atoms,

$R^2 - R^7$  are each, independently, H or an  
 alkyl group, preferably having 1-4 carbon  
 atoms, and

15

$R^8$  is an alkylene group, preferably having  
 3-6 carbon atoms.

In a preferred embodiment, the present  
 photographic materials have incorporated therein a  
 dye-forming colour coupler. Such couplers are well  
 known and are often incorporated in photographic  
 materials as a dispersion in droplets of a coupler  
 solvent.

20

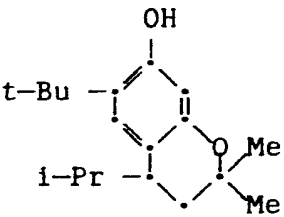
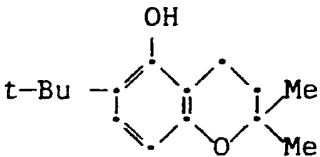
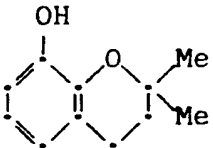
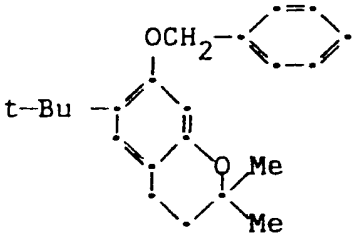
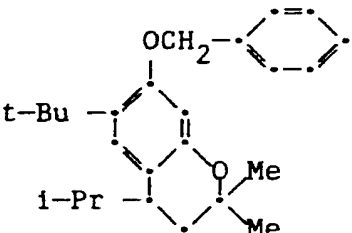
Examples of chromanol compounds useful in the  
 present invention are listed in the following Table.

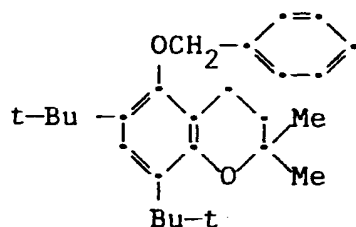
25

30

35

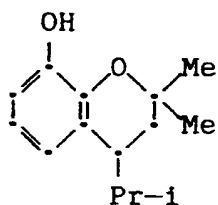
TABLE 1

	Compound	Compound No.
5		(I)
10		(II)
15		(III)
20		(IV)
25		(V)
30		
35		



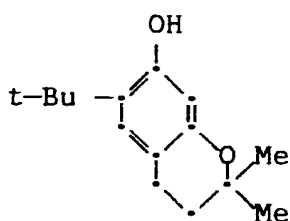
(VI)

5



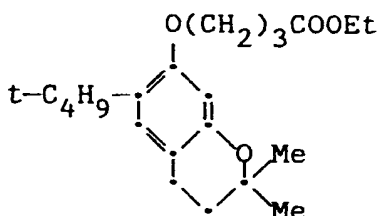
(VII)

10



(VIII)

15



(IX)

20

The chromanols employed in the present invention may be prepared by reaction of the appropriate dihydric phenol with the appropriate diene, eg 2,5-dimethyl-2,4-hexadiene to form the basic chromanol followed by other reactions, in themselves known, to introduce a further substituents. Such processes are illustrated in Examples below.

25

The chromanols are used in an amount sufficient to stabilize the photographic image dyes and their precursors e.g. in an amount from 0.2 to 2.0 mole per mole coupler, more preferably at approximately equimolar amounts.

30

35

The chromanol may be incorporated in the silver halide emulsion layer or a layer adjacent thereto. It can be incorporated as a separate dispersion, but is preferably incorporated in admixture with the coupler. Both coupler and stabilizer may be dissolved in a conventional coupler solvent, such as dibutyl phthalate. As in the production of ordinary coupler dispersions, a volatile and/or water-miscible auxiliary solvent, such as ethyl acetate, may be used to aid the dispersion process and then removed by evaporation or by washing the set dispersion. Also, the dispersion process can be assisted by the presence of a surface active compound, as usual in the manufacture of coupler dispersions.

In the following discussion of suitable materials for use in the emulsions and elements of this invention, reference will be made to Research Disclosure, December 1978, Item 17643, published by Industrial Opportunities Ltd., The Old Harbourmaster's, 8 North Street, Emsworth, Hants PO10 7DD, U.K., the disclosures of which are incorporated herein by reference. This publication will be identified hereafter as "Research Disclosure". References giving information on couplers and on methods for their dispersions are given in Sections VII and XIV, respectively, of Research Disclosure.

The couplers which may be employed in the present photographic materials are water-insoluble compounds containing ballast groups, phenolic (including naphtholic) couplers being used for producing cyan dyes, acylacetanilides for yellow dyes and pyrazolones for producing magenta dyes. Patents describing couplers for use in the present invention include the following United States Patents:

-6-

## Cyan dye-forming

3 367 531	3 034 892
2 423 730	3 311 476
2 474 293	3 419 390
2 772 826	3 458 315
2 895 826	3 476 563

5

## Magenta Dye forming

2 343 703	3 062 653
2 369 489	3 127 269
2 600 788	3 311 476
2 908 573	3 419 391
2 933 391	3 518 429

10

## Yellow dye-forming

2 298 443	3 277 155
2 407 210	3 408 194
2 875 057	3 415 652
2 908 573	3 447 928
3 265 506	3 933 501

15

20 An account of dye-forming development is given in  
'Modern Photographic Processing', Vol. 2, Grant Haist,  
Wiley, New York, 1978, Chapter 9.

25 The stabilizers are useful in any  
coupler-incorporated silver halide photographic  
materials, including monochrome materials,  
false-colour materials and colour transparency,  
negative and print materials, to stabilize the image  
dye obtained on development with a solution including  
a p-phenylenediamine colour developing agent. Such  
30 developing agents are well-known, being described  
in, for example Photographic Processing Chemistry,  
L.F.A. Mason, Focal Press, London, 2nd edition (1975)  
pp 229-235 and Modern Photographic Processing, Grant

35



Haist, Wiley, New York (1979), Volume 2 pp 463-8.

They may also be used in colour materials not containing couplers but processed in developer solutions containing couplers.

5 The silver halide emulsion employed in the elements of this invention can be either negative-working or positive-working. Suitable emulsions and their preparation are described in Research Disclosure Sections I and II and the publications cited therein. Suitable vehicles for the emulsion layers and other layers of elements of this  
10 invention are described in Research Disclosure Section IX and the publications cited therein.

The photographic elements of this invention or individual layers thereof, can contain brighteners (see Research Disclosure Section V), antifoggants and  
15 stabilizers (see Research Disclosure Section VI), antistain agents and image dye stabilizer (see Research Disclosure Section VII, paragraphs I and J), light absorbing and scattering materials (see Research Disclosure Section VIII), hardeners (see Research  
20 Disclosure Section XI), plasticizers and lubricants (see Research Disclosure Section XII), antistatic agents (see Research Disclosure Section XIII), matting agents (see Research Disclosure Section XVI) and development modifiers (see Research Disclosure Section  
25 XXI).

The photographic elements can be coated on a variety of supports as described in Research Disclosure Section XVII and the references described therein.

30 Photographic elements can be exposed to actinic radiation, typically in the visible region of the spectrum, to form a latent image as described in Research Disclosure Section XVIII and then processed

to form a visible dye image as described in Research Disclosure Section XIX. Processing to form a visible dye image includes the step of contacting the element with a colour developing agent to reduce developable silver halide and oxidize the colour developing agent. Oxidized colour developing agent in turn  
 5 reacts with the coupler to yield a dye.

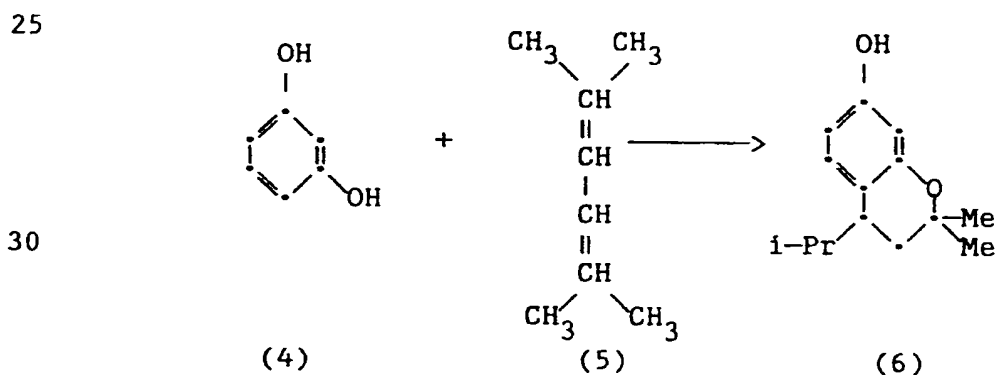
With negative working silver halide emulsions this processing step leads to a negative image. To obtain a positive (or reversal) image, this step can be preceded by development with a non-chromogenic  
 10 developing agent to develop exposed silver halide, but not form dye, and then uniform fogging of the element to render unexposed silver halide developable. Alternatively, a direct positive emulsion can be  
 15 employed to obtain a positive image.

Development is followed by the conventional steps of bleaching, fixing, or bleach-fixing, to remove silver and silver halide, washing and drying.

The following Examples are given for a better understanding of the invention.

20 EXAMPLE 1

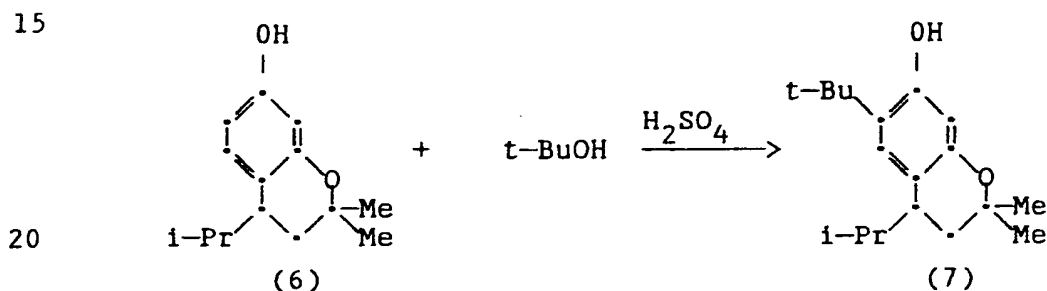
Preparation of 2,2-dimethyl-4-isopropyl-7-hydroxy-3,4-dihydro-benzopyran (6).



Resorcinol (11.0g, 0.1m), petroleum ether (b.p. 60–80°) (2ml) and orthophosphoric acid (5mls) were stirred at room temperature. To the stirred mixture 2,5-dimethyl-2,4-hexadiene (11.0g, 0.1m) was added dropwise (1/2 hr) keeping the temperature of the reaction mixture between 30–35°C. After refluxing the reaction for 8 hrs. it was poured into ice/water, extracted with ethyl acetate, dried and evaporated to dryness. The 7-chromoanol (6) was obtained in 89% yield by column chromatography.

#### EXAMPLE 2

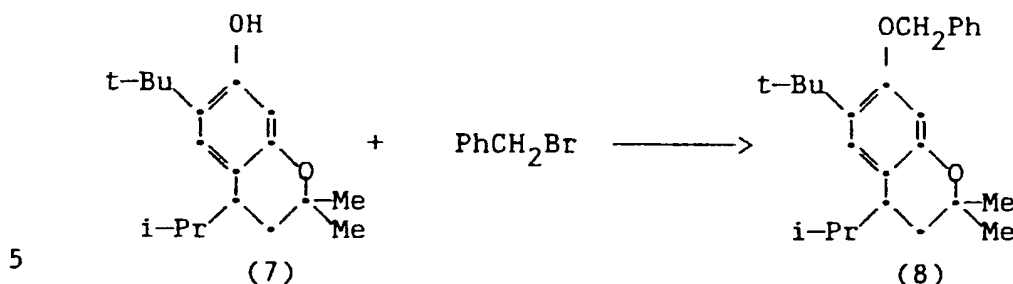
Preparation of 2,2-dimethyl-4-isopropyl-6-t-butyl-7-hydroxy-3,4-dihydrobenzopyran (7).



To a stirred mixture of the 7-chromoanol (6) (4.38g, 0.2m) and t-butanol (10ml), sulphuric acid (5ml) was added dropwise keeping the temperature of the reaction mixture between 25–30°C. The reaction mixture was stirred at room temperature for 3 hrs, then poured onto ice/water. The solid was filtered and crystallised from aqueous ethanol to afford the butylated chromanol (7) (4.4g, 85%).

#### EXAMPLE 3

Preparation of 2,2-dimethyl-4-isopropyl-6-t-butyl-7-benzyloxy-3,4-dihydrobenzopyran (8).



To a stirred mixture of 7-chroman-7-ol (7), (5.5g, 0.2m) and potassium carbonate (5gms) in acetone (30ml), benzylbromide (3.42g, 0.2m) was added. The reaction mixture was refluxed with stirring for 18 hrs. The reaction mixture was poured onto ice/water, extracted with ethyl acetate, dried and evaporated to afford a lemon-yellow solid. Crystallisation from aqueous ethanol gave the required product (6.6g, 90%).

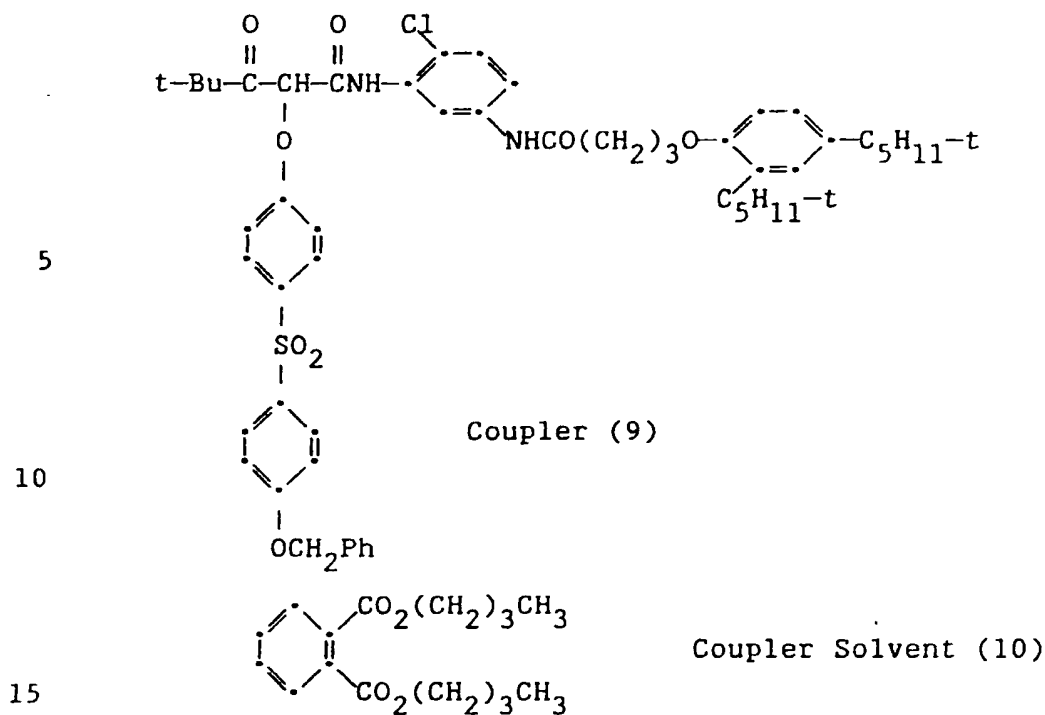
#### 15 EXAMPLE 4

##### Yellow dye light stability improvement

Single layer film strips were prepared by coating a gel-subbed polyethylene-terephthalate support with a photosensitive layer containing a silver bromiodide emulsion at  $0.398 \text{ Ag/m}^2$ , gelatin at  $1.36 \text{ g/m}^2$  and dispersion of coupler (9) in coupler solvent (10) (1.5 moles/mole of coupler). The coupler coverage was  $0.83 \text{ millimoles/m}^2$ . The photographic layer was overcoated with a layer containing gelatin at  $3.0 \text{ g/m}^2$  and bis-vinylsulphonylmethylether hardener at 1.5 weight percent based on total gelatin. Similar coatings were prepared using coupler dispersions which also contained one of the stabilisers (I) and (V) at 0.5 mole per mole coupler.

Samples were exposed through a graduated density test object and developed with 4-amino-3-methyl-N-ethyl-N-β-(methanesulphonamido)ethyl-aniline in an EP-2 process.

-11-



Patches from each coating having a density at or above 1.0 were faded for 6 weeks using a 5.4 klux xenon source, the UV component of which was removed by a coating of Tinuvin 328 (Trade Mark of Ciba-Geigy) in a gelatin dispersion at a coverage of 750 mg/m<sup>2</sup> on a transparent support. The loss in transmission optical density at the wavelength of maximum absorption was measured. The data is presented below in Table 2.

-12-

TABLE 2

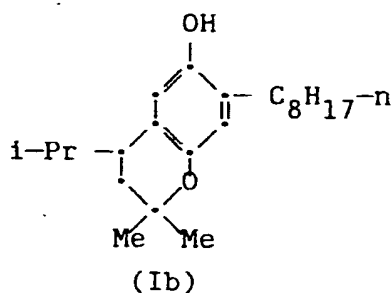
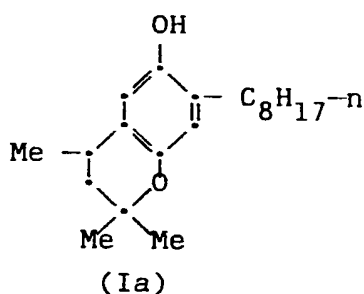
Stabiliser	Fade Time	Strip 1		Strip 2	
		Init dens	Fade	Init dens	Fade
5 nil	6 wks	1.01	0.15	0.98	0.08
I	6 wks	1.08	0.04	1.34	0.03
V	6 wks	1.12	0.03	1.19	0.05

10 The presence of Stabiliser compounds (I) and (V) greatly improved the fade performance in all cases.

EXAMPLE 5 (Comparative)

15 In a comparative experiment, coatings were prepared as described in Example 4, except that the test materials included in the coupler dispersion were the 6-chromanols (Ia) and (Ib). The results of the fade experiments showed that these 6-chromanols greatly reduced the stability of the yellow image dye as shown in Table 3 below.

20 Compounds Ia and Ib were as follows:



-13-

TABLE 3

	Coating	Initial Density	Final Density	Density Loss
5	Coupler (9)	1.05	0.97	-0.08 (7.6%)
	Coupler (9) + Compound Ia	1.09	0.52	-0.57 (52%)
10	Coupler (9) + Compound Ib	1.16	0.85	-0.31 (27%)

EXAMPLE 6Magenta dye light stability improvement

15 Typical single layer film strips were prepared by coating, as in Example 4, a gel-subbed polyethylene- terephthalate support with a photosensitive layer containing a silver bromiodide emulsion at  $0.538 \text{ Ag/m}^2$ , gelatin at  $3.23\text{g/m}^2$  and dispersion of coupler (11) in coupler solvent (10) (2.8 moles/mole of coupler) and the test material (1.0 mole/mole of coupler). The photographic layer was overcoated with a layer containing gelatin at  $1.08\text{g/m}^2$  and bis-vinylsulphonylmethylether hardener at 1.0 weight percent based on total gelatin. In this case the test materials used were stabilisers (II) and (VII), and a reference coating containing no stabiliser was also prepared.

25 Samples were exposed and tested as in Example 4 but using a Wratten (Trade Mark) 2B filter instead of the Tinuvin coating. The results are tabulated below.

Coupler (11) had the formula:

-14-

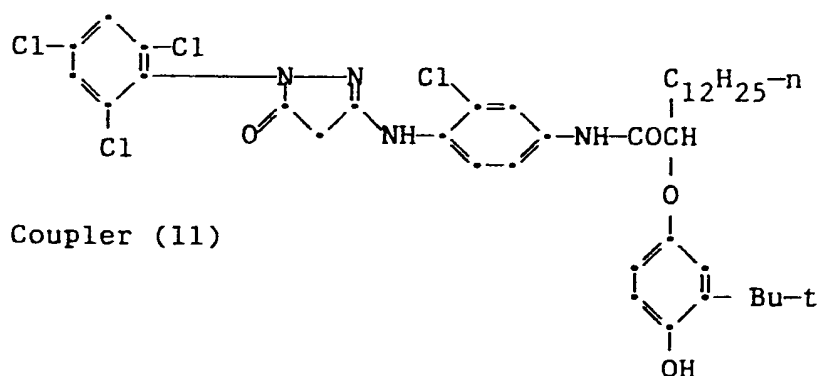


TABLE 4

15

Stabiliser	Fade Time	Strip 1		Strip 2	
		Init dens	Fade	Init dens	Fade
nil	6 wks	1.05	0.10	1.37	0.10
II	6 wks	0.96	0.06	1.38	0.06
VII	6 wks	0.98	0.05	1.36	0.05

20

The presence of Stabiliser compounds (II) and (VII) greatly improved the fade performance in all cases.

25

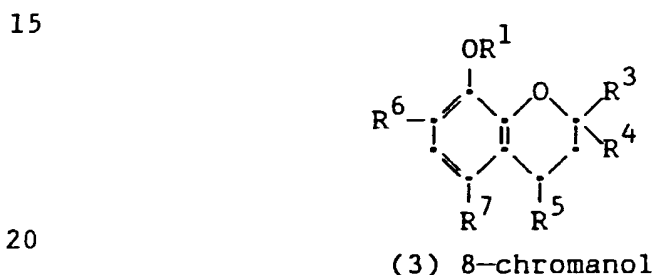
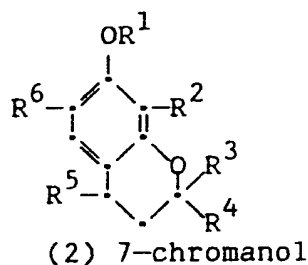
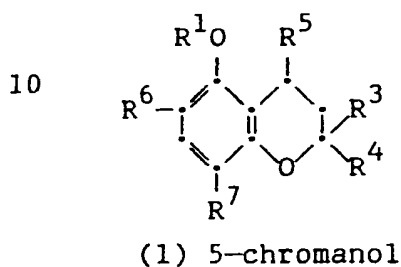
30

35



## CLAIMS:

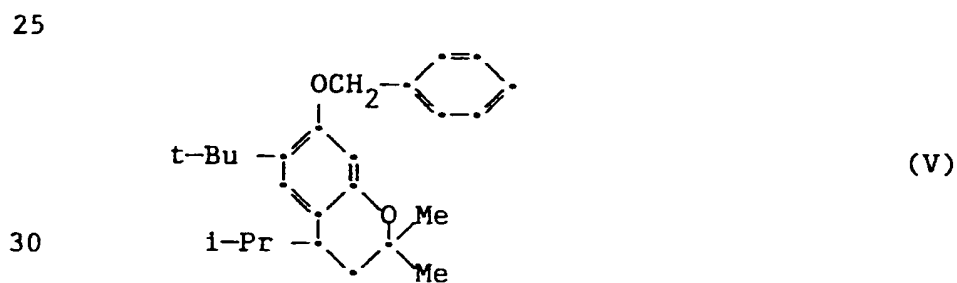
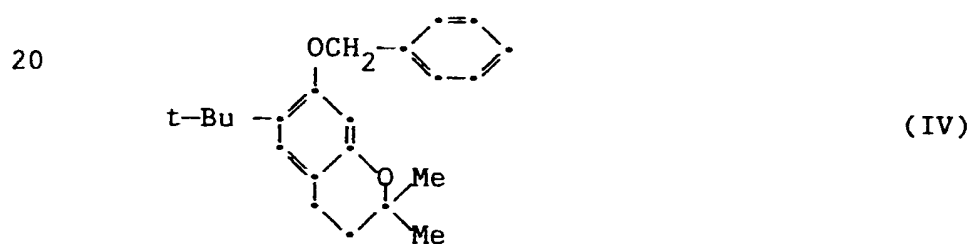
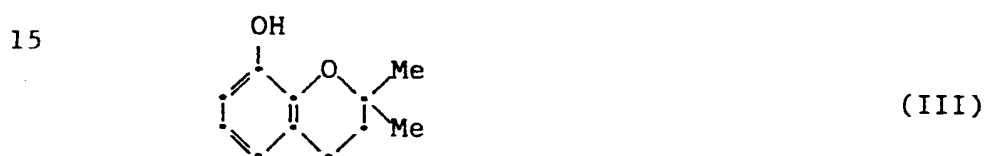
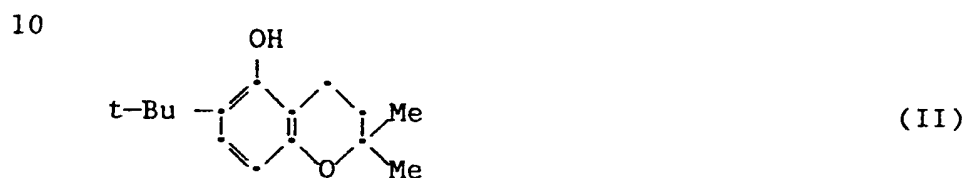
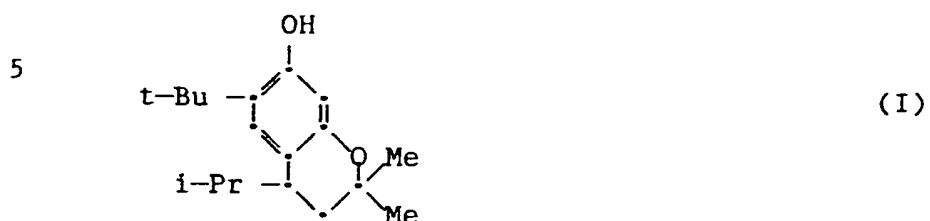
1. A colour photographic material comprising a support carrying at least one photographic silver halide emulsion layer having associated therewith a 5-, 7- or 8-chromanol image dye stabiliser.
2. A photographic material as claimed in claim 1 in which the chromanol compound has one of the formulae:



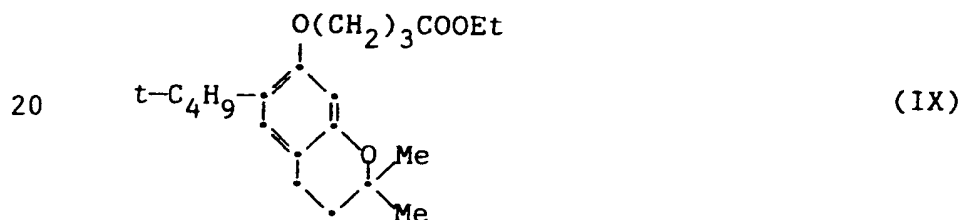
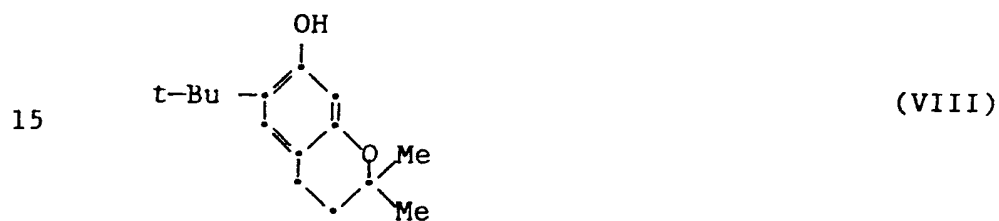
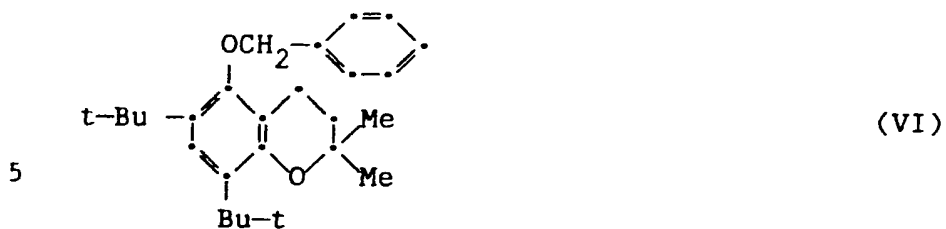
wherein  $R^1$  is H, alkyl, substituted alkyl (including arylalkyl), or  $-R^8-COOR$ ,  
 $R$  is an alkyl,  
 $R^2 - R^7$  are each, independently, H or an alkyl group, and  
 $R^8$  is an alkylene group,.

3. A photographic material as claimed in claim 2 in which the alkyl groups of claim 2 contain from 1-4 carbon atoms.
4. A photographic material as claimed in any of claims 1-3 which also contain a photographic colour coupler.

5. A photographic material as claimed in any of claims 1-4 in which the chromanol is selected from one of the following:



-17-



25 6. A method of preparing a 5-, 7- or 8-chromanol comprising the reaction of the appropriate dihydric phenol with the appropriate diene.

7. A method as claimed in claim 6 in which the diene is 2,5-dimethyl-2,4-hexadiene.

30

35

# INTERNATIONAL SEARCH REPORT

International Application No PCT/EP 91/00068

<b>I. CLASSIFICATION OF SUBJECT MATTER</b> (if several classification symbols apply, indicate all) <sup>6</sup> According to International Patent Classification (IPC) or to both National Classification and IPC IPC5: G 03 C 1/34, 7/392														
<b>II. FIELDS SEARCHED</b> <div style="text-align: right; margin-right: 100px;">Minimum Documentation Searched<sup>7</sup></div> <table style="width: 100%; border: none;"> <tr> <td style="width: 20%; border: none;">Classification System</td> <td style="border: none;">Classification Symbols</td> </tr> <tr> <td style="border: 1px solid black; height: 40px; vertical-align: bottom;">IPC5</td> <td style="border: 1px solid black; height: 40px; vertical-align: bottom;">G 03 C</td> </tr> </table> <div style="text-align: center; margin-top: 5px;">Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in Fields Searched<sup>8</sup></div>			Classification System	Classification Symbols	IPC5	G 03 C								
Classification System	Classification Symbols													
IPC5	G 03 C													
<b>III. DOCUMENTS CONSIDERED TO BE RELEVANT<sup>9</sup></b> <table border="1" style="width: 100%; border-collapse: collapse;"> <thead> <tr> <th style="width: 10%;">Category *</th> <th style="width: 60%;">Citation of Document,<sup>11</sup> with indication, where appropriate, of the relevant passages<sup>12</sup></th> <th style="width: 30%;">Relevant to Claim No.<sup>13</sup></th> </tr> </thead> <tbody> <tr> <td style="text-align: center; vertical-align: top;">Y</td> <td style="vertical-align: top;">JP, A, 61-158331 (KONISHIROKU PHOTO KK) 18 July 1986, see page 307 &amp; Orbit Search Service, File WPAT, Accession number 86-228719/35, (KONISHIROKU PHOTO KK), J61158331-A, 860718, 8635, abstract  --</td> <td style="text-align: center; vertical-align: top;">1,2,3</td> </tr> <tr> <td style="text-align: center; vertical-align: top;">Y</td> <td style="vertical-align: top;">US, A, 4155765 (MITSUTO FUJIWHARA ET AL) 22 May 1979, see column 3  --</td> <td style="text-align: center; vertical-align: top;">1,2,3</td> </tr> <tr> <td style="text-align: center; vertical-align: top;">A</td> <td style="vertical-align: top;">US, A, 4623617 (YUTAKA KANEKO ET AL) 18 November 1986, see column 69, line 60 - line 65  --</td> <td style="text-align: center; vertical-align: top;">1-7</td> </tr> </tbody> </table>			Category *	Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>	Relevant to Claim No. <sup>13</sup>	Y	JP, A, 61-158331 (KONISHIROKU PHOTO KK) 18 July 1986, see page 307 & Orbit Search Service, File WPAT, Accession number 86-228719/35, (KONISHIROKU PHOTO KK), J61158331-A, 860718, 8635, abstract  --	1,2,3	Y	US, A, 4155765 (MITSUTO FUJIWHARA ET AL) 22 May 1979, see column 3  --	1,2,3	A	US, A, 4623617 (YUTAKA KANEKO ET AL) 18 November 1986, see column 69, line 60 - line 65  --	1-7
Category *	Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>	Relevant to Claim No. <sup>13</sup>												
Y	JP, A, 61-158331 (KONISHIROKU PHOTO KK) 18 July 1986, see page 307 & Orbit Search Service, File WPAT, Accession number 86-228719/35, (KONISHIROKU PHOTO KK), J61158331-A, 860718, 8635, abstract  --	1,2,3												
Y	US, A, 4155765 (MITSUTO FUJIWHARA ET AL) 22 May 1979, see column 3  --	1,2,3												
A	US, A, 4623617 (YUTAKA KANEKO ET AL) 18 November 1986, see column 69, line 60 - line 65  --	1-7												
<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>* Special categories of cited documents:<sup>10</sup></p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance, the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance, the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"&amp;" document member of the same patent family</p> </div> </div>														
<b>IV. CERTIFICATION</b> <table style="width: 100%; border: none;"> <tr> <td style="width: 50%; border: none;">Date of the Actual Completion of the International Search</td> <td style="width: 50%; border: none;">Date of Mailing of this International Search Report</td> </tr> <tr> <td style="border: 1px solid black; height: 40px; vertical-align: bottom;">25th March 1991</td> <td style="border: 1px solid black; height: 40px; vertical-align: bottom; text-align: center;">19. 04. 91</td> </tr> <tr> <td style="border: none;">International Searching Authority</td> <td style="border: none;">Signature of Authorized Officer</td> </tr> <tr> <td style="border: 1px solid black; height: 40px; vertical-align: bottom; text-align: center;">EUROPEAN PATENT OFFICE</td> <td style="border: 1px solid black; height: 40px; vertical-align: bottom; text-align: center;">F.W. HECK </td> </tr> </table>			Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	25th March 1991	19. 04. 91	International Searching Authority	Signature of Authorized Officer	EUROPEAN PATENT OFFICE	F.W. HECK				
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report													
25th March 1991	19. 04. 91													
International Searching Authority	Signature of Authorized Officer													
EUROPEAN PATENT OFFICE	F.W. HECK													

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category *	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No
A	US, A, 4254216 (TAKASHI UCHIDA ET AL) 3 March 1981, see column 23, line 50 - line 65  --	1-7
A	US, A, 4863842 (YUTAKA KANEKO ET AL) 5 September 1989, see column 37, line 1 - line 20  --	1-7
A,P	US, A, 4906559 (TOYOKI NISHIJIMA ET AL) 6 March 1990, see column 45, line 1 - line 35  --  -----	1-7

**ANNEX TO THE INTERNATIONAL SEARCH REPORT  
ON INTERNATIONAL PATENT APPLICATION NO.PCT/EP 91/00068**

SA 43560

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.  
The members are as contained in the European Patent Office EDP file on 28/02/91  
The European Patent office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A- 4155765	22/05/79	AU-B- 503973	27/09/79
		AU-D- 2735477	01/02/79
		DE-A-B-C 2734148	02/02/78
		FR-A- 2360914	03/03/78
		GB-A- 1583780	04/02/81
		JP-C- 1274339	31/07/85
		JP-A- 53017729	18/02/78
		JP-B- 59052421	19/12/84
		SE-A- 7708529	01/02/78
US-A- 4623617	18/11/86	EP-A-B- 0178165	16/04/86
		JP-A- 61241755	28/10/86
		JP-A- 61090156	08/05/86
		JP-A- 61158330	18/07/86
US-A- 4254216	03/03/81	AU-B- 511995	18/09/80
		AU-D- 3960778	13/03/80
		CA-A- 1136470	30/11/82
		DE-A-C- 2839434	15/03/79
		FR-A-B- 2402892	06/04/79
		GB-A-B- 2004078	21/03/79
		JP-C- 1092186	16/04/82
		JP-A- 54048538	17/04/79
		JP-B- 56024257	04/06/81
		SE-A- 7809422	13/03/79
		US-A- 4314011	02/02/82
US-A- 4863842	05/09/89	EP-A-B- 0240568	14/10/87
		JP-A- 62178964	06/08/87
		WO-A- 87/01826	26/03/87
		JP-A- 62096944	06/05/87
US-A- 4906559	06/03/90	DE-A- 3605279	28/08/86
		JP-A- 61194444	28/08/86

For more details about this annex : see Official Journal of the European patent Office, No. 12/82